Resetting microstructures and properties in TRIP-assisted advanced high strength steels
by
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Abstract

Metals are widely used structural materials in automotive, packaging, construction, and machines. Driven by demands to decrease greenhouse gas emissions, the reuse, re-forming, and re-manufacturing of metals draws great attention. However, current processes such as mechanical joining, welding, coating, etc. have key practical and theoretical limitations. Recently, a new reuse strategy is proposed, which aims to reset the microstructures of materials to maintain performance and increase lifetime. We refer to alloys that demonstrate this capability as resettable alloys. One resettable alloy is the transformation-induced plasticity-maraging (TRIP-maraging) steel. However, current resettable TRIP-maraging steels require long and unfeasible resetting treatments. The limit of resetting kinetics has not been reached and the microstructure resetting mechanism has not been fully understood. Here we focus on providing a deeper understanding of the resetting mechanism in TRIP-maraging steel, such as the effects of composition and pre-strain, to increase the kinetics of the underlying transformations. This study demonstrates that with proper microstructure design, the resetting process could be completed within minutes following a critical level of deformation.

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Chapter 1

Introduction

1.1 Motivation

Metals are the most widely used structural materials in the world [1]. They provide a large range of strength-ductility combinations with relatively low manufacturing costs. Nevertheless, the metal production industry is also one of the largest carbon dioxide emission sources [2]. Full process analysis demonstrates that with no precautions in current steel production, the amount of carbon dioxide emission will double by 2050 (figure 1-1). Even with process solutions (e.g. increasing fuel usage efficiency and decreasing yield loss), carbon dioxide emissions could at best be kept constant. To decrease carbon dioxide emissions, a combination of process optimization and materials design solutions are required. However, commercial reuse processes are typically either direct reuse or involve mild modification. Current high performances metals, which typically have complicated processing [3] and structure [4], are not designed to be healed or reused, and the performance of reused parts is not guaranteed. Thus, we need to explore materials design approaches to increase the reuse, re-forming, and re-manufacturing capability of metals.
1.2 State of the art

Currently, reparation of structural components can fall into two categories: post-crack reparation and pre-crack reparation (figure 1-2). The former type attempts to heal metals after a macro-scale crack appears. The macro-crack inside the component cannot be repaired autonomously, and an external evaluation system is required to detect cracks. Cracks are typically closed by mechanical joining or welding, depending on the damage situation, cost, and other boundary conditions. Mechanical joining using extra fixtures can be used to provide a compression stress field to close the crack [5, 6, 7]. However, the repaired components are more vulnerable to failure since the microstructures of components are not repaired. In the welding approach [8], additive materials are melted at damaged area and fill the crack by surface tension. Because of the high temperature, the substrate forms strong chemically bonds with the filling materials and provides a higher final strength compared with mechanical joining [9, 10, 11, 12]. The reparation quality depends on the composition and microstructure of additive materials, the welding environment, and the heating source [13, 14].

Pre-crack reparation focuses on healing micro-cracks and the damaged microstructure. The reparation of the microstructure can be executed autonomously or non-autonomously. Non-autonomous reparation typically involves extra microstructural analysis for damage evaluation. Stress relief annealing, one type of non-autonomous
reparation strategy, focuses on decreasing defect density and residual stress of metals by a low temperature heating process [15]. Self-healing is an autonomous approach to achieve microstructure reparation [16, 17]. The strategy used here is to close nano-scale voids or refill macro-cracks by adding a second phase [18] or built-in filling agents[19, 20, 21]. Given that the self-healing agent could autonomously locate and heal cracks, external damage evaluation is unnecessary, which simplifies the component reuse process drastically. Shape memory alloys (SMA) are used as a second phase in a self-healing material [18]. When the crack reaches the SMA phase, the tip stress field will trigger the phase transformation of the SMA. The volume fraction then changes due to the phase transformation and introduces a counter stress field to close the crack tip. In aluminum alloys, second phase precipitates are applied as infill agents[19]. At elevated temperature, precipitates concentrate around and inside micro-voids, which have higher energy, and close the crack. However, a second phase or infill agent is required to achieve self-healing, and the microstructure of the material changes when the phase transformation or the filling process is triggered. This
will end up changing the final performance of the material, and the properties are not always improved. In addition, the fraction of self-healing components defines material’s lifetime. When all of the second phase is transformed or all of the fillings are used, the material will finally fail. Thus, it induces a trade-off between part lifetime and performance, which is not preferred.

1.3 Concept

Recently, a new non-autonomous pre-crack reparation method, microstructure resetting, has been proposed [22]. Instead of healing cracks, the resetting strategy focuses on regenerating the intrinsic damage toughness of materials. During the lifetime of a component, the synergistic effects of time, temperature, environment and working conditions cause an irreversible evolution of component microstructure (e.g. dislocation accumulation, environment elements penetration, and corrosion, etc.). The properties of the material, which was able to fulfill it service requirements, irreversibly deteriorate, followed by failure. If the material is designed in such a way that the microstructure deterioration during service is reversible, components could maintain their damage toughness at a high level and infinitely delay failure.

The feasibility of microstructure resetting is based on the damage characteristics. Intuitively, macro-cracks, high-density micro-cracks, and large shape changes are hard to repair under a microstructure resetting scenario; Micro-scale damages (e.g. micro-voids, precipitates, second phases, interstitial elements, phase transformations and dislocation cells), are the most resettable damages. Luckily, many damage types (e.g. fatigue [23, 24, 25], thermal embrittlement (TE) [26], wear [27], hydrogen embrittlement (HE) [28], radiation damage [29], and stress corrosion cracking [30]) have localized crack distributions and small shape changes, which provides a great opportunity for resetting (figure 1-3) [31]. Nevertheless, different failure mechanisms and metal systems have different failure histories and damage characteristics. The resetting approaches could be completely different for different systems, while still following the same microstructure reversion concept.
The resettable material proposed is TRIP-maraging steel for static loading failure. Quasi-static loading damage includes strain hardening, voids and cracks, which will decrease the toughness of the material. Depending on the material type, the void and strain hardening distribution changes from sparse to dense, and shape change crosses over from small to large (martensitic steel [32], IF steel [33]). TRIP-maraging steel consists of a metastable phase, which has transformation induced plasticity (TRIP), and an age-hardened martensite phase (maraging), which has high strength by nano precipitation (figure 1-4) [34]. The resetting treatment proposed is a simple heat treatment, which is based on the energy difference between martensite and austenite phase. At elevated temperature, the austenite phase has lower Gibbs free energy, which activates the back transformation of the strain-induced martensite phase. The intermetallic precipitates in the original martensite matrix are hard to dissolve or grow at the resetting temperature. The precipitates pin dislocations inside martensite and prevent ferrite formation [34]. In summary, when the material deforms, the austenite transforms to martensite; after resetting, the strain induced martensite transform back to austenite. In the maraged martensite, the deformation process increases dislocation density and the resetting process decreases it to original level.
This study provides a guideline for designing alloys to achieve microstructure resetting (figure 1-5). For single-phase systems (blue circles), crystal recovery, crystallization, and controlled phase transformation could achieve microstructure resetting. For multi-phase systems (red circles), which constitute the majority of steels, resetting is more difficult. Simply applying heat treatment on current steels will not reset their microstructures. Dual phase steels consist of a ferrite matrix and martensite islands in ferrite grain boundaries. When heat treatment is applied, the soft ferrite goes through recovery and recrystallization, which will reset the ductility of the material. However, the martensite phase will be softened by dislocation annihilation and carbide precipitation and even decomposition [3]. A material design approach is
required to increase the stability of the hard phase while maintaining the reversibility of the soft phase in current steel systems. Thus, with similar resetting methods, the hardness of the hard phase is maintained even at elevated temperature; the original phase and defect level of soft phase are reproduced through recovery or back transformation.

1.4 Challenges

In TRIP-maraging steel, resetting performances depends on the interactions between the precipitates and dislocations in martensite phase and the back transformation of strain-induced martensite to austenite at elevated temperature. Current studies highlight the microstructure reversion; however, the related mechanism has not been studied. In addition, the current resetting process follows the same treatment used for producing this material, which requires 8 hours annealing time. The limit of resetting kinetics has not been reached.

There are three austenite reversion mechanisms in steel systems: segregation-induced martensite to austenite reversion [34, 35, 36], short-range diffusion-assisted grain nucleation and growth, and martensitic transformation [37, 38, 39]. Segregation-induced reversions are typical in martensitic steel systems, where boundary segrega-
tions of alloying elements takes place at elevated temperature. The other austenite reversion mechanisms, short-range diffusion and shear reversion, are dependent on alloying elements and annealing process. For carbon steel (e.g. Hadfield steel), in order to revert, an austenite annealing temperature in the austenite region is required [40, 3] and reversion is diffusional. For stainless steel, austenite reversion is a commonly used method to obtain ultra-fine austenite grains, where diffusional austenite nucleation and growth take place. In Mn steel, the ability of martensitic reversion depends on heating rate[41], pre-strain [37], and the Gibbs free energy difference between austenite and martensite [38], etc.

In order to increase the kinetics of resetting, the goal is to promote the shear reversion mechanism during austenite formation. The limitations of shear reversion resetting are considered based on pre-strain, composition and heating temperature in this paper. Then, the effects of shear reversion on reset microstructure and mechanical properties are studied. Finally, a resetting strategy based on fast reversion is proposed in TRIP-maraging system.
Chapter 2

Methodology

2.1 Material design and processing

2.1.1 Material processing

TRIP-maraging steels have composition of Fe-9Mn-3Ni-1.4Al-0.01C (mass %) [34]. They are cast and hot rolled at 1100 °C, and then homogenized at 1100 °C for one hour followed with a water quench. The as-quenched (AQ) steels have fully martensite microstructures. Then AQ steels are cold rolled from about 5 mm to about 1.5 mm (about 70% thickness reduction). Thus, we have cold-rolled (CR) martensite. Then an annealing process is applied, which will allow Mn segregate into martensite boundaries. Then martensite phases partially revert to austenite phase, forming a two-phase microstructure [34]. A box furnace with air environment is used here. The CR TRIP-maraging steels are obtained by annealing from CR state at 600 °C for one hour (figure 2-3). In order to protect sample surface from oxidation during heat treatment, the sample is sealed inside glass tubes with argon environment (figure 2-1). The glass tubes used here are quartz tubes, which have enough geometric stability at 600 °C and low pressure. The tube is firstly melted to close one end. Then the samples are placed inside the tube. The mechanical pump pumps out the air inside the tube and then high purity argon gas is pumped in. The pumping and venting process is repeated at least three times to remove oxygen. Then the other end of the
tube is sealed with hydrogen flame. In order to keep samples at room temperature, a water bath is applied at the end of glass tube where the sample sit.

After deformation, samples are reset via heat treatment. The annealing at 600 °C (5 min to 60 min) is applied to samples with different strain levels. The furnace is preheated to 600 °C and then the sample is inserted to achieve a high heating. After annealing, the sealed sample is directly water quenched to room temperature.

![Glass tube sealing](image)

**Figure 2-1: Glass tube sealing**

### 2.1.2 Thermodynamic calculation

The final phase structure and element distribution is analyzed through Thermo-Calc [42]. Thermo-Calc is able to calculate all kinds of thermodynamic equilibrium calculations (e.g. phase equilibrium, phase transformation, and grain boundary movements etc.) for all alloying systems based on a thermodynamic database. Here, we calculate the elemental distribution heterogeneity between the austenite and martensite phases with composition Fe-9Mn-3Ni-1.4Al-0.01C (mass %). As shown in figure 2-2, the composition of the BCC and FCC phases at different temperature is calculated. Specifically, at 600 °C (annealing temperature) the equilibrium composition of the austenite phase is 16% Mn, 5.7% Ni, 0.86% Al. Then the martensite starting temperature (Ms), austenite starting temperature (As) and austenite finishing temperature (Af) for each phase are calculated based on an experimental equation [43] (table 2.1).

<table>
<thead>
<tr>
<th>Phase</th>
<th>Austenite °C</th>
<th>Martensite °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ms</td>
<td>-23</td>
<td>502</td>
</tr>
<tr>
<td>As</td>
<td>455</td>
<td>683</td>
</tr>
<tr>
<td>Af</td>
<td>642</td>
<td>910</td>
</tr>
</tbody>
</table>

Table 2.1: Transformation temperature calculated by experimental equation for two phases
Figure 2-2: Predicted chemical composition of FCC phase as a function of temperature. Calculation performed using Thermo-Calc.

2.2 Material characterization

Two approaches has been used to analyze material characteristics: quasi-in-situ and post-mortem (figure 2-3). For each approach, samples are first annealed to achieve a two phase microstructure. Then the samples are deformed to different strain levels. For post-mortem processes, samples are deformed to fracture, while for the other approach, deformation is stopped before 10\% strain. A digital image correlation tool is applied to analyze the strain. Since samples and loading conditions are symmetric in the plane perpendicular to the loading direction, the surface strain represents the bulk strain at each cross section, when boundary effects are neglected. Then deformed samples are annealed to reset their microstructure. At each stage, tools like X-ray diffraction (XRD) and scanning electron microscope(SEM) are employed for microstructure analysis, which will be explained in detail in the following paragraph. Specifically, for post-mortem analysis, the strain of samples are changing along the tensile direction. The inspection areas are chosen non-uniformly distributed along the loading axis based on local strain. For the in-situ approach, assuming the sample is also uniformly deformed, an average strain in the uniformly deformed area is used.
as local strain.

There are difficulties of in-situ resetting analysis during resetting. When heated at 600 °C, even though the sample is sealed with argon in a glass tube, the sample surface is oxidized because of residual oxygen, which direct surface analysis impossible. In addition, the average grain size of austenite is smaller than 1 μm (figure 3-2), making austenite even vulnerable to oxidation [44]. Thus, the inspection area before and after heat treatment is always different.

2.2.1 Mechanical test

To study the mechanical properties and resettability of TRIP-maraging steel, a uniaxial tensile test is conducted with a strain rate around $5 \times 10^{-4}$ /s. The dog-bone shape
(figure 2-4) tensile samples are cut along the rolling direction by electrical discharge machining (EDM). EDM cuts samples by igniting an electric arc between the cutting wire and the parts. When samples are locally heated up above melting temperature, cutting happens. The gauge length of the sample is 4 mm and the thickness is 1.5 mm. Then samples are ground and polished on all surfaces to remove the surface oxide layer. After that, the exact geometries of samples are measured by caliper. Here a Gatan deformation stage (Duban) is used to control the uniaxial tensile test of the sample. In order to capture the local strain level of the sample, digital image correlation is used. Firstly, white paints are applied uniformly onto the sample surface to provide a uniform background. Then black dots, with a size around 20 pixels and a widely distributed histogram (figure 2-5), are applied by air brush. During deformation, a high resolution camera captures images of samples with a frame rate of 0.5/s. These dots work as tracking marks of the sample surface. By measuring the position changes of the dots, we could calculate the surface strain (figure 2-6). Here, for batch analysis, an open-source software (GOM correlate) is used, from which we obtain the surface strain at each point as well as an average strain in the gauge area.

2.2.2 Microstructure analysis

Samples go through different deformation routes and are analyzed at each stage, i.e. undeformed, deformed and reset. Different analysis tools are used (e.g. X-ray diffrac-
Digital image correlation (XRD), DTA, scanning electron microscope (SEM) etc.) which will be explained in detail in the following paragraphs. In order to capture the original grain characteristics and prevent the influence of surface topography and any oxidization layer, samples are ground and polished before analysis. Firstly, the sample is ground using grinding paper of 300, 500, 800, 1000, and 1200 mesh (American unit) sequentially to remove its surface oxide layer and end up with a sample with fine surface grinding traces and a shallow deformation layer, which is caused by previous grinding history. Then the sample is polished using a 3 \( \mu \text{m} \) diamond suspension for 5 min. Then the OPS suspension is used for the final polishing for around 15 to 20 min.

To obtain phase volume fraction quantitatively, X-ray diffraction (XRD) is used via Bruker D8 with general area detector diffraction system (GADDS). The X-ray source used is Cu \( K_\alpha \) with 0.5 mm spot size. The sample stage has 6 dimensions of freedom
with a laser pointer to align the position. With a CCD camera inserted, we are able to position the X-ray beam into the area of interest and record the beam position for future analysis. The sample and detector is placed at certain positions to guarantee a $\theta$-$2\theta$ relationship with X-ray incident direction. The Vantec-2000 X-ray detector is a two-dimensional detector, which has resolution of 2048 x 2048 pixels. This detector can capture the Ewald diffraction of samples, which provides information like lattice type, texture, strain, etc. By transforming this signal, we could also obtain general diffraction pattern. Here we use $2\theta$ varies from 30 to 90 degree with step size of 15 degree and a 300 s pattern capture time.

The microstructure of the material is analyzed using the SEM, Tescan and Merlin with different electron detectors. The secondary electron (SE) detector is used to capture surface topography information. When the incidence angle of the electron is high, i.e. the electron is focused on the peak of the surface, the SE signal is strong and we have a bright contrast in SE image. Vice-versa, the valley on the surface will have a dark contrast [46].

The back-scattered electron (BSE) detector provides images with surface topography contrast, elemental concentration contrast and diffraction contrast. Specifically, the diffraction contrast plays an important role, which means it shows the difference between atoms at difference diffraction conditions. By tilting the sample in an certain way, we could reach a position where the electrons diffract into the grain without deflection. Thus, electron channeling contrast imaging (ECCI) is obtained. This image provides more diffraction information, such as crystal structure, orientation and defects. For example, precipitates in the matrix change the atom arrangement around it, thus changing the local diffraction pattern. Then this area shows a different diffraction contrast compared with matrix. Thus, precipitates show as black dots in a white background and as white dots in a black background, under different channeling conditions. Similarly, stacking fault defects show a rectangle [47], where one side is a white gradient, and one side is a black line in a dark background. Dislocations are represented as a combination of one white line and one black line.

The electron backscatter diffraction (EBSD) detector captures the backscatter
diffraction pattern (kikuchi pattern) of the region, where the electron beam is focused. This pattern provides a detailed information of crystal structure and orientation [37]. The results obtained by EBSD are analyzed by Orientation Imaging Microscopy (OIM\textsuperscript{TM}) system. From the analysis, we could get phase information, orientation information, grain boundary characteristics, lattice distortion, texture, etc. The grain is assigned as a region where lattice misorientation is less than 5°. The image quality (IQ) map shows the pattern quality at each scanning point, which could be caused by lattice distortion (defects), extra alloying elements (elemental segregation), surface topography, etc. Kernel average misorientation (KAM) shows the lattice misorientation compared with its neighbor (second neighbor) area. Thus, KAM shows more about plastic deformation and residual strain inside one grain. In addition, the characteristics of grain boundaries are defined by the grain orientation relationship.

The energy dispersive X-ray spectroscopy (EDS) could capture the X-ray that is generated from electron activation caused by electron beam. Each element has its special X-ray spectra, and elemental concentration is proportional to signal intensity. A line scan is applied on the sample to analyze the elements distribution.
Chapter 3

Results

3.1 Original characteristics

CR TRIP-maraging steels are formed via partial transformation during annealing (one hour at 600 °C). The annealing process allows redistribution of alloying elements to different phases and the formation of metastable austenite at room temperature. The EBSD phase map (figure 3-2-a) shows that the CR TRIP-maraging steel contains a martensite matrix (red) and unevenly distributed austenite between martensite boundaries (green). The austenite grains in densely distributed regions typically have an equiaxed shape. The austenite grains in sparsely distributed area typically have an acicular shape and smaller grain sizes. Figure 3-2-b shows the orientation map in the austenite grains, where each color represents one orientation direction relative to external coordinate system. Figure 3-1 shows the special Kurdjumov-Sachs (K-S) boundaries in all martensite-austenite boundaries. A K-S boundary is a special boundary where the grain orientation matches the following relationship [48]: {111} || {110}, <T10>||<T11> The austenite grains in CR TRIP-maraging steels have K-S relationship with at least one neighboring martensite grain. Considering possible orientation combinations, the variants of austenite with K-S relationship to certain martensite, is 24 [35]. From the orientation map, austenite grains show no preferred variant, and the orientation is randomly distributed (in densely distributed region).
Figure 3-1: K-S boundary in all martensite-austenite boundaries

Figure 3-2-c shows an EDS line scan of an austenite grain in an enlarged area (yellow rectangular) of figure 3-2-a. The small graph shows the composition distribution along the line. The y-axis is the EDS signal intensity of manganese (Mn), nickel (Ni) and aluminum (Al) with arbitrary units, where high intensity means high concentration. The peak in Mn spectra (Mn enrichment) matches the austenite grain area. Other elements (Al and Ni) show no preference under current testing conditions and resolution. The enrichment of Mn in the austenite phase helps stabilize the austenite to achieve two-phase structure at room temperature[34].

An in-situ deformation test is applied on the CR TRIP-maraging sample. Figure 3-2-d,e shows a zoom-in area (black rectangle) in figure 3-2-a, before and after 5% global deformation. The austenite grain in the top middle of figure 3-2-d completely transforms to martensite in figure 3-2-e. Several austenite areas close to grain boundaries transform to a black area, which means that the confident indexes of these areas are lower than 0.1 (out of 1). One explanation is that the austenite phases are in the middle of phase transformation and the kikuchi pattern could not be recognized as either a austenite lattice or a martensite lattice. In addition, more martensite boundaries appear, such as in the left top area, which are caused by deformation and
rotation of martensite grains.

Figure 3-2-f shows the images of austenite inside the blue rectangle in figure 3-2-d,e before and after 5% deformation. The whole grain is not in the same orientation before deformation, as the contrast inside the austenite is not uniform. After 5% strain, all of the austenite grains are in the same channeling condition (similar contrast), and more stacking faults appear, which are the bright white lines in the same direction. This is caused by the rotation and deformation of austenite phase. Figure 3-8-a,b shows the BSE image of CR TRIP-maraging steel before and after deformation at different areas. At 0% strain, austenite has a low stacking fault density and some grains have annealing twins[3]. As strain increases, we see stacking faults at different slip planes inside one austenite grain, which results from dislocation movements.

In order to study the deformation mechanisms of CR TRIP-maraging steels at different strain levels, post-mortem analysis is applied. This sample, which is uniaxially deformed, shows a yield strength of 950 MPa, a ultimate stress of 1000 MPa, a uniform elongation of 12.8% and a total elongation to failure of 28% (figure 3-4).
Then EBSD analysis is applied along the deformation axis (orange dots in figure 3-4). With strain level increase across the sample, the austenite fraction decreases from 35% to 0%. When the strain level is smaller than 7%, there is less transformation taking place (5%). Most plastic deformation comes from dislocation movement [49]. When strain increased but before necking strain (12.8%), 24% austenite transformed to martensite (68.5% of total austenite fraction). In this region, plasticity comes from austenite transformation (TRIP effect). In addition, there is a region preference. As figure 3-3-a shows, the untransformed austenite localized at certain martensite band. After necking, plasticity deformation is localized, and most austenite grains around the necking area transform into martensite.

![Deformed and Reset EBSD Images](image)

**Figure 3-3:** EBSD images of post-mortem sample at different strain levels and after resetting treatment

### 3.2 Microstructure resetting

#### 3.2.1 Critical resetting strain

In order to find the critical resetting strain of CR TRIP-maraging steels, post-mortem resetting treatments are applied. After a 15 min resetting treatment, EBSD measure-
ments are carried out in areas with different amounts of pre-deformation (figure 3-3-b). As mentioned, the orange dots in figure 3-4 show the austenite fraction after uniaxial deformation. The blue dots in figure 3-4 show the austenite fraction after resetting. Thus, the graph could be separated into three parts: the untransformed austenite region, which is dark green; the reversible austenite region, which is light green; and the irreversible austenite region, which is red.

The deformation level before resetting influences the fraction of resettable austenite. When strain is smaller than 12%, most of the strain-induced martensite grains transform to austenite, and the austenite fraction returns to 30%. However, there is a minimum austenite loss after resetting, which is around 3%. One explanation is the decrease of total Mn concentration of the sample during heat treatment. When temperature is high, Mn is vulnerable to oxidization, which decreases the austenite stability and the maximum austenite volume fraction. In addition, analysis is carried on the surface of the sample, where the Mn loss is significant. When the pre-strain level is higher, the fraction of reversible austenite grains increases. However, more austenite grains are transformed to compromise the plastic strain, the irreversible austenite fraction increases and the total austenite fraction decreases. In addition, there is also a region preference for reverted austenite grains (figure 3-3-b). In some areas, the austenite fraction is higher than 50%; while in other areas, the austenite fraction is lower than 5%. When the strain level is extremely high (> 40%), the increase in the resettable austenite fraction is much smaller. In addition, there is a maximum amount of resettable austenite fraction. This is because activation energy is not enough to compromise the elastic strain caused by phase transformation. A higher resetting temperature or longer segregation process is required in order to achieve full reversion [34, 50].

### 3.2.2 Resetting feasibility

In order to apply enough deformation while still at a range where fully microstructure resetting is achievable, here deformation is keep below 10%. However, the strain level of the sample is calculated through a DIC analysis after the tensile test is finished,
as the pre-strain of the resetting is hard to control.

One resetting condition used here is 600 °C heat treatment for one hour followed by water quenching, which is the same as the annealing condition during materials formation. As shown in figure 3-5-a, the strength of the material keeps increasing while the ductility of the material slowly decreases under one hour resetting treatments. The original material shows a yield stress of 900 MPa, and the deformation is stopped at a strain level of 8%. After resetting, yield stress decreases to 880 MPa, and the deformation is stopped at a strain level of 6%. After four repetitions of the deformation-resetting process, yield strength increases to 950 MPa, and the uniform deformation strain decreases to 7.5% compared to original state (12.8% in figure 3-4). The total elongation decrease to 11.5% (28% in figure 3-4).

Another resetting condition is 600 °C heat treatment for 15 minutes followed by water quenching. The sample is firstly uniaxially deformed to 8.8% strain. Then the resetting process is applied. The yield points of the material were kept constant (1000 MPa). The hardening effect increases after resetting, and the ultimate strength in-
creases (from 1050 MPa to 1100MPa). The total elongation to fracture after resetting kept at 24%, compared with 28% total elongation of other samples (figure 3-4).

Figure 3-6 and figure 3-7 show the phase evolution of the CR TRIP-maraging steel during deformation and resetting. The deformation is stopped at strain level 8.8%. The resetting process takes 15 min. From the phase map (figure 3-6-a,b,c), the austenite fraction decreases and increases. However, there is a decrease in grain size in the EBSD map. From the KAM map (figure 3-6-d,e,f), where the brighter color means higher the Kernel average misorientation. We could see an increase after deformation and a decrease after resetting. This means the lattice distortion increases by deformation and decreases by resetting. In the martensite phase, lattice distortion represents the dislocation density. Noting that the KAM average of the reset microstructure is higher than the undeformed microstructure, which means the martensite is hardened.

Figure 3-8 shows the BSE image of CR TRIP-maraging steel during the deformation and resetting process at different areas. In order to obtain high quality BSE images, a small field of view is applied. Here, the microstructure of a single grain acts as a representation of typical grains characteristics. The austenite grain in figure 3-
8-a,b,c is shown as a white area with a clear grain boundary. The black-white stripes represent stacking fault inside the austenite. The stacking fault density is low in the undeformed state (only three in one grain). After deformation, the austenite in the middle has stacking faults at differently planes (with stripes in both vertical and horizontal directions). After resetting, the austenite's stacking fault density decreases to its original value (only two inside right grain). Martensite in figure 3-8-d,e,f is shown as a dark area without a clear boundary. Since the martensite always has residual stress inside the grain [51], it is hard to find an area where the channeling condition is the same for the whole grain. For the martensite at an undeformed stage, there are more dislocations (shown as white lines) and precipitates (white dot). After the deformation, the dislocation density increases, just through image analysis, while the precipitates stay the same. In addition, the dislocations are typically cross-linked and pinned by precipitates. After the resetting treatment, the dislocations are still cross-linked.
3.2.3 Resetting mechanism

The kinetics of the resetting reversion is much higher than the segregation reversion process. As shown in figure 3-9, the x-axis is time and y-axis is austenite fraction, which is calculated from the EBSD phase map. The blue dots represent the sample in a cold rolled state and the orange dots represent the sample that is severely deformed (>60%) from the original state. Both samples are annealed at 600 °C for different times. For the cold rolled sample (blue dot), the amount of reverted austenite linearly increases with heat treatment time. However, in severely deformed sample, there is a big jump at very beginning. After 5 min heat treatment, there is around 20% austenite reverted.

Figure 3-10 shows the BSE and EBSD images of the sample in figure 3-9, which is annealed 15 min from severely deformed state. In figure 3-10-a, the austenite grain in the middle of the image has a lath shape and stacking faults inside (black lines). In the corresponding EBSD phase map, the austenite grain has low image quality. The surrounding martensite has a different channeling condition, as the contrast in the BSE image is different. This means the orientation inside martensite grain is not uniform, which is also shown in the EBSD IPF map. If we calculate the KAM
of the martensite around newly formed austenite, we could see a high KAM index around the austenite phase, representing a stress concentration. In figure 3-10-b, the austenite in the center right has grain size around 1 μm (the average austenite size of the CR TRIP-maraging steel). However, the dislocation density inside the grain is extremely high. We could see high density stacking faults along a certain direction in the middle of the austenite grain, while the right corner of the austenite shows no defect contrast in the current channeling condition. Figure 3-10-c shows the austenite grain with clear boundary and low defects.

Figure 3-8: BSE images of austenite and martensite phases of TRIP-maraging steel at different stages
Figure 3-9: Austenite reversion fraction of cold rolled martensite and deformed TRIP-maraging
Figure 3-10: BSE and EBSD images of austenite at the middle stage of reversion
Chapter 4

Discussion

4.1 Resetting feasibility of CR TRIP-maraging steel

In CR TRIP-maraging steel, the austenite phase is formed by annealing at 600 °C, after cold rolling at fully martensite phase\[52\]. Before annealing, the material has no heterogeneous elemental distribution. The annealing segregation assisted the partial reversion of austenite from the martensite matrix. Because of the increase in boundary density by cold rolling, the annealing time is one hour, which is much shorter than typical segregation annealing process \[52\]. After annealing, as seen from the EDS line scan (figure 3-2-c), Mn is enriched in the austenite phase. The cold rolled martensite shows a random grain boundary distribution \[52\], which influences the reversion austenite characteristics. The severe deformation caused by cold rolling destroys the austenite memory effect during reversion \[35\]. Although the K-S relationship is maintained, austenite grains show no orientation preference (figure 3-1, figure 3-2-b). However, the preference of austenite nucleation sites \[53\] exist in CR TRIP-maraging steel(figure 3-2-c). Austenite grains typically form at areas with more boundaries and high misorientation angles.

The newly formed austenite modifies the martensite matrix and achieves different microstructure with better performances \[36, 52\]. The alloying elements change the stacking fault energy of austenite to a range where the TRIP effect is possible \[49, 54\]. The austenite grains show widely distributed stability and a high strain hardening
rate, which is influenced by grain shape, grain size, alloying elements [55, 56, 54]. Chiang reported the equiaxed austenite tends to transform at lower strain, which represents a high work hardening rate at the beginning but drops much faster than the laminated austenite [57]. Lee reported that the ultra-fine grains have higher stability compared to large austenite grains [58]. The martensite phase here is ductile martensite, which is softened during the tempering recovery process and hardened by intermetallic precipitates [59]. Because of the long aging time and low alloying elements concentration, the CR TRIP-maraging steel shows a UTS around 1 GPa, which is lower than Ni-based maraging steel. During deformation, there is dynamic strain partitioning between the two phases [34], which is based on dislocation movements and phase transformations. At the beginning of the deformation (around yield point), almost no phase transformation happens (figure 3-4). During the in-situ deformation test, only one austenite grain transforms at 5% strain (figure 3-2-d). The dislocation movements cause the increase in defect density (figure 3-6) (e.g. stacking fault density increase in the austenite phase in figure 3-8-b and the dislocation density increase in the martensite phase in figure 3-8-e). Only austenite at the low boundary density area, which typically have acicular shape (figure 3-2-a), is transforming. When the strain and stress reach a critical value, TRIP takes place, showing a sharp increase in transformed austenite. In addition, the higher the strain level, the more austenite transforms (figure 3-4). This also means that most austenite has similar stability. The untransformed austenite are localized in certain areas, where martensite boundary density is high (figure 3-3-b). When strain is higher than 22%, the martensite transformation rate decreases until all the austenite is consumed (figure 3-4).

The annealing process highly influences the resetting performance of the material. A previous study of AQ TRIP-maraging steel shows great dependence of the first annealing time (figure 4-1) [22]. AQ TRIP-maraging steel shows great resetting properties when both the segregation annealing process and the resetting annealing process last for 8h. The stress strain curve of original and reset materials are almost on top of each other (figure 1-4-c). However, if both segregation annealing and resetting annealing decrease to one hour, the performances of the reset annealing materials
is far away from the original state (figure 4-1). The yield strength and the UTS of the material decrease after each resetting annealing. The resetting annealing resembles the segregation annealing of AQ TRIP-maraging steel, where the strength decreases with extended annealing time [34]. This means that if the segregation annealing process is not complete, the segregation process continues during the following resetting annealing process. In addition, the resetting time is much shorter than the segregation annealing time, in order to allow extra segregation to take place. Thus, the resetting reversion and segregation reversion should follow different transformation mechanisms in order to have different kinetics under same condition.

4.2 Resetting kinetics

The resetting of CR TRIP-maraging steel further proves this idea (figure 3-5). Here, we keep the segregation annealing time the same while decreasing the resetting annealing time from one hour to 15 min. The resttability of the materials is maintained and the recovery of ductility appears for both cases, which supports the complete reversion of austenite phase. Especially in the 15 min resetting case, the engineering stress strain curve shows identical yield strength and the final elongation is 24%. Given that the soft austenite defines the yield point and ductility of this system, the resetting of austenite phase under 15 min is complete (figure 3-6). The increase in UTS shows an incomplete recovery of martensite, which is also shown in the EBSD map, where the average KAM of the martensite grain increases (figure 3-6).

In addition, there is a limitation in the maximum amount of austenite that could be achieved in 15 min resetting, which is dependent on pre-strain and the deformation mechanism. Current studies demonstrate that the cold rolling strain influences the formation of reverted austenite [37, 60] in austenitic stainless steel. When the strain level is below 50%, and the strain-induced martensite maintains its lath geometry, the reverted austenite forms the same structure of austenite laths and blocks. When lath martensite structure is completely destroyed by cold rolling, equiaxed austenite nucleates at random boundaries of martensite matrix. As figure3-4 shows, when the
strain level increases, the amount of irreversible austenite increases, which corresponds to the deformation of strain-induced martensite, which increases the reversion energy barrier. From figure 3-9, the reverted austenite fraction reaches a maximum (around 20% of austenite could revert back) within 5 min and is kept static even when time is increased to 15 min. The reversion ability of austenite in a short time shows the time independence, which is a typical characteristic of shear reversion.

![Stress-Strain Curve](image)

Figure 4-1: AQ TRIP-maraging steel with both segregation and resetting annealing time for one hour

### 4.3 Austenite reversion mechanism

For resetting reversion of CR TRIP-maraging steel, all three reversion mechanisms are possible. However, in the short time resetting condition, shear reversion is the dominate mechanism. Given that room temperature deformation does not change the elements distribution [61], the strain-induced martensite still has Mn enrichment inside the grain (figure 3-2). In addition, Mn segregation is limited by the annealing temperature, annealing time, and current elemental gradients. Even from the CR state, where there is no Mn gradient and there is a high dislocation density (figure
3-9), only 5% austenite forms after 15 min 600 heat treatment. Thus, the effect of long range diffusion is negligible during resetting. However, if the Mn gradient is not high enough (this happens when the first segregation annealing is not complete) and the resetting time is long, the segregation reversion will cause great change in the reset material (figure 4-1, figure 3-5 one case).

![Diagram of continuous heating transformation with different reversion mechanisms](image)

**Figure 4-2:** Schematic diagram of continuous heating transformation with different reversion mechanisms [41]

Distinguishing short-range diffusion nucleation and shear reversion is a challenge, since both have high kinetics and require no long-range diffusion time. Currently, in-situ technologies, such as EBSD [62], high energy XRD [63], confocal laser scanning microscopy (CLSM) [64], are used to identify shear reversion. The independence of the transformation temperature from heating rate in DSC analysis is one typical characteristic of shear reversion. When heating rates are low, the austenite starting temperature increases with increased heating rate, showing a diffusion controlled phase transformation characteristic. When the heating rate is high enough, transformation starting and ending temperatures remain at a constant value, which is higher than the low heating rate Ac1 temperature (figure 4-2) [41]. The most commonly used method is based on microstructure characteristics. The microstructure of diffusive
and displacive austenite is also very different (figure 4-3) [38]. If the transformation is martensitic, the newly formed austenite has high dislocation density and stacking fault density. In addition, the grain size is similar to the original austenite grain size. Then the following recovery and recrystallization within high stacking fault austenite grains forms defect-free austenite grains [39]. If the reversion is diffusion, only small austenite grains inside the martensite matrix with low defect density appear.

![Illustration of two types of austenite reversion mechanism](image)

Here we use ECCI tools to analyze the microstructural characteristics of reset austenite. However, considering the transformation rate of shear reversion, it is almost impossible to stop the annealing just after martensitic transformation finished, especially when in-situ analysis is unavailable. If we stop at the final state of austenite reversion, all the microstructure is the defect-free austenite (figure 3-8 end stage). The only possible solution will be stopping at the middle stage of reversion. If stress-induced martensite phase goes through the upper route, there will be large austenite grains with high stacking fault density and partial recovery inside the grains. As figure 3-10-b shows, newly formed austenite has the same grain size as the original austenite but with an extremely high stacking fault density. In addition, the shear
reversion is fast, and the recrystallization of the high defect density austenite starts to recrystallize. Thus, we could see inside the austenite grain, where there is discontinuity of the stacking faults, which represents recrystallization. In addition, in figure 3-10-c, the austenite is fully recovered in half of the grain.

In sum, the resetting mechanism of CR TRIP-maraging steel is dominated by martensitic phase transformation followed with crystallization. When the recovery process is not complete, the mechanical response of the material changes (increase in YS and UTS). However, the total elongation of the material is reset to the original state, which corresponds to the full reversion of austenite phase.
Chapter 5

Conclusion

In this work, a successful resetting of TRIP-maraging steel (combining transformation-induced plasticity and martensite age hardening) is achieved, which is proved by microstructure characterization, such as electron back-scattered diffraction (EBSD) and electron channeling contrast imaging (ECCI). The reset steels keep same yield strength and ductility and a 5% increase in strength.

The success of resetting is based on the two-phase microstructure. The precipitate-pinned martensite and Mn-enriched austenite is maintained. Shear reversion is the dominant mechanism in short time resetting. However, when the resetting time is longer, elemental diffusion introduces great instability in material performances.

The current 15 min resetting process causes an increase in strength, which is because of incomplete recovery of martensite. There is a limit in shear reversion under 600 °C resetting, when the strain level is high. When the strain exceeds critical value, strain-induced martensite will plastically deform, which reduces its shear reversibility.

The microstructure stability of the original state influences the resetting feasibility. In order to reset the mechanical properties, a long annealing time at the material formation process is critical, which will create a stable Mn gradient to prevent further segregation.

An increase in the resetting kinetics relies on martensitic austenite reversion. If the shear reversion process does not reach phase equilibrium at the resetting temperature, segregation transformation follows. The shear reverted austenite has high stacking
fault density and the following recovery is necessary to maintain the strength and ductility of materials.
Chapter 6

Future Work

The reversion of austenite during the resetting process is confirmed on CR TRIP-maraging steel. However, there is still controversy over the real reversion mechanism. Here, we mainly use images to prove the shear reversion mechanism and the following understanding is limited: the effect of Mn segregation during the first annealing process on the reversion process is limited by the resolution of EDS analysis; the deformation effect over the strain-induced martensite and how it influences reversion mechanisms; the preference of austenite nucleation on boundary characteristics.

To clarify these points the following technology can be used: Differential scanning calorimetry (DSC) analysis could provide the exact phase transformation temperature and the effect of heating rate. An in-situ study of the reversion process, to see where the new austenite forms and the kinetics of newly formed austenite to gather with TEM-EDS to get composition influences; in-situ high energy XRD analysis to get the phase transformation and lattice strain release during resetting.

For wider studies as mentioned, there are three challenges: defining the critical resetting point, designing the resetting process and materials to achieve full reversion of microstructure; decreasing the time and cost of resetting process to make it more feasible. In order to broaden the material system and different failure conditions of resetting, more fundamental works need to be done (e.g. failure analysis and alloying design) in order to define the resettability and increase the resettability of the material. For example, wear is gradual surface removal under abrasive loading. The main
failure mechanism is surface hardening and lamination. From current studies of wear failure, the strain hardening rather than the absolute strength influences the wear resistance of the surface. Then the resetting process would base on removing surface roughness and recovering surface hardening. Fatigue refers to the time-delayed fracture of materials subjected to cyclical stresses below the yield point. There is almost no shape changes in material lifetime (only crack tip plasticity take place). Damages for resetting here are typically localized void and persistent slip band. Hydrogen embrittlement (HE) is the deleterious effects that hydrogen in several forms has on the mechanical properties of materials. The resetting requirement would be hydrogen enrichment. Similar are thermal embrittlement (TE), which typically is caused by segregation and decomposition, and radiation damage, which refers to deleterious effects from radiation, including cavity, swelling. Damages are secondary phases and extra alloying elements rather than the strain-induced microstructure deterioration.
Bibliography


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